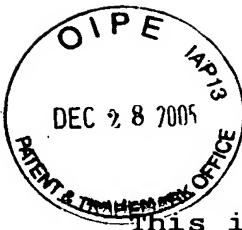


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[Inventor]

 [Address or Residence] c/o Seiko Epson Corporation,
 3-5, Owa 3-chome, Suwa-shi,
 Nagano-ken

 [Name] Hiroshi KATO

[Inventor]

 [Address or Residence] c/o Seiko Epson Corporation,
 3-5, Owa 3-chome, Suwa-shi,
 Nagano-ken

 [Name] Nobuhiro MIYAKAWA

[Applicant]

 [Identification No.] 000002369

 [Name or Appellation] Seiko Epson Corporation

[Agent]

 [Identification No.] 100095728

 [Patent Attorney]

 [Name or Appellation] Masataka KAMIYANAGI

 [Telephone No.] 0266-52-3139

[Assigned Agent]

 [Identification No.] 100107076

 [Patent Attorney]

| | | |
|--------------------------|-------------------|---|
| [Name or Appellation] | Eikichi FUJITSUNA | |
| [Assigned Agent] | | |
| [Identification No.] | 100107261 | |
| [Patent Attorney] | | |
| [Name or Appellation] | Osamu SUZAWA | |
| [Indication of Fee] | | |
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[Title of the Invention] TONER AND IMAGE-FORMING APPARATUS
USING THE TONER

[Claims]

[Claim 1] A toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles, and (3) a process of externally adding positively electrifiable silica fine particles.

[Claim 2] A toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles, (3) a process of externally adding positively electrifiable silica fine particles, and (4) a process of externally adding particles comprising a long chain fatty acid or a salt thereof.

[Claim 3] A toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide

fine particles, and (3') a process of externally adding positively electrifiable silica fine particles, and particles comprising a long chain fatty acid or a salt thereof.

[Claim 4] The toner as claimed in any of claims 1 to 3, wherein the negatively electrifiable silica fine particles comprise two kinds of negatively electrifiable silica fine particles each having a different average particle size, and the addition ratio of the negatively electrifiable silica fine particles having a large average particle size to the negatively electrifiable silica fine particles having a small average particle size is 1/3 to 3/1 in a mass ratio.

[Claim 5] The toner as claimed in any of claims 1 to 4, wherein the titanium oxide fine particles and positively electrifiable silica fine particles are externally added in a mass ratio of from 1/3 to 3/1.

[Claim 6] The toner as claimed in any of claims 1 to 5, wherein the titanium oxide fine particles are rutile-anatase type titanium oxide fine particles.

[Claim 7] An image-forming apparatus which is stocked with the toner as claimed in any of claims 1 to 6.

[Claim 8] The image-forming apparatus as claimed in claim 7, which is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a

toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a toner which is used for developing an electrostatic latent image in electrophotography, electrostatic recording and electrostatic printing and for forming an image by thermal fixation, and also relates to an image-forming apparatus using the toner.

[0002]

[Background Art]

The toner for forming electrostatic images generally comprises, as the toner mother particles, fine particles of a binding resin containing a coloring component, e.g., a dye or a pigment, and, if necessary, an electrification controlling agent, and the toner is manufactured by a method of adding external additives to the outside (surface) of the toner mother particles for the purpose of providing flowability or controlling an electrification property. As the external additives, positively

electrifiable silica fine particles, negatively electrifiable silica fine particles, inorganic fine particles other than silica (e.g., titanium oxide), fatty acid metal salt and the like are used.

[0003]

For example, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles and inorganic fine particles having a low electrical resistance value (e.g., metallic oxide inorganic particles, e.g., titanium oxide) (these toners are disclosed in patent literature 1 and 2), and a toner comprising toner mother particles having externally added thereto two kinds of positively electrifiable substances (e.g., silica) each having different particle size and inorganic fine particles (patent literature 3) are known. In patent literature 1 to 3, negatively electrifiable binding resins are used.

[0004]

Also, a toner being externally adding positively

electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles to a toner mother particle (refer to, e.g., patent literature 4), and a toner having a excellent charge rising property which is produced by a method of externally adding a first component, a second component, a third component and a fourth component to toner mother particles at the same time, or externally adding the first component lastly, taking hydrophobic silica fine particles or hydrophobic titania as the first component, hydrophobic silica fine particles or hydrophobic titania having larger particle sizes than the particle sizes of component 1 as the second component, inorganic fine particles as the third component, and a fatty acid metal salt as the fourth component (refer to, e.g., patent literature 5) are known.

[0005]

Further, there is disclosed in a patent literature a method to obtain a toner in which the liberation of external additives is restrained by externally adding in the order of titanium oxide fine particles and silica fine particles to toner mother particles (refer to, e.g., patent literature 6).

[0006]

However, in the toners obtained by the methods disclosed in patent literature 1 to 6, external additives

(positively electrifiable silica fine particles, negatively electrifiable silica fine particles, titanium oxide fine particles and the like), which function to control electrification or flowability, are liable to be desorbed from the surface of the toner, which causes the reduction of flowability or electrification property of the toners, as a result, transfer efficiency and image density are depressed.

[0007]

[Patent literature 1]

JP-A-2000-267337 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

[Patent literature 2]

JP-A-2002-14487

[Patent literature 3]

JP-A-2002-214834

[Patent literature 4]

JP-A-11-231571

[Patent literature 5]

JP-A-2001-100452

[Patent literature 6]

JP-A-2002-72544

[Patent literature 13]

JP-A-2002-202622

[0008]

[Problems to be Resolved by the Invention]

An object of the present invention is to provide a toner which is low in desorption of external additives (e.g., positively electrifiable silica fine particles, negatively electrifiable silica fine particles, titanium oxide fine particles and the like), can maintain the electrification property for a long period of time, shows high flowability and transfer efficiency, and is not accompanied by the reduction of image density.

[0009]

[Means of Solving the Problems]

The present invention provide a novel toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles, and (3) a process of externally adding positively electrifiable silica fine particles.

[0010]

The present invention also provide a novel toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing

a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles, (3) a process of externally adding positively electrifiable silica fine particles, and (4) a process of externally adding particles comprising a long chain fatty acid or a salt thereof.

[0011]

The present invention further provide a novel toner which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles, and (3') a process of externally adding positively electrifiable silica fine particles, and particles comprising a long chain fatty acid or a salt thereof.

[0012]

In a preferred embodiment of the present invention, the negatively electrifiable silica fine particles comprise two kinds of negatively electrifiable silica fine particles each having a different average particle size, and the addition ratio of the negatively electrifiable silica fine particles having a large average particle size to the negatively electrifiable silica fine particles having a small average particle size is 1/3 to 3/1 in a mass ratio.

[0013]

In another preferred embodiment of the present invention, the titanium oxide fine particles and positively electrifiable silica fine particles are externally added in a mass ratio of from 1/3 to 3/1.

[0014]

In a still preferred embodiment of the present invention, the titanium oxide fine particles are rutile-anatase type titanium oxide fine particles.

[0015]

The present invention also relates to an image-forming apparatus which is stocked with any toner as described above.

[0016]

In a preferred embodiment of the present invention, the image-forming apparatus is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[0017]

[Detailed Description of the Preferred Embodiment]

The toner of the present invention is manufactured by adding materials, e.g., negatively electrifiable silica fine particles, positively electrifiable silica fine particles, titanium oxide fine particles, and particles comprising a long chain fatty acid or a salt thereof to toner mother particles in a specific order. In the specification of the invention, materials externally added to toner mother particles, e.g., negatively electrifiable silica fine particles, positively electrifiable silica fine particles, titanium oxide fine particles, and particles comprising a long chain fatty acid or a salt thereof are referred to as external additives, and adding these external additives to the exteriors (surfaces) of toner mother particles is called external addition.

[0018]

The materials which are used in the invention, e.g., (i) toner mother particles and the materials constituting the toner mother particles (so-called internal additives, e.g., binding resins, colorants, mold releasing agents, dispersants, electrification controlling agents, and magnetic agents), (ii) negatively electrifiable silica fine particles, (iii) positively electrifiable silica fine particles, (iv) titanium oxide fine particles, (v) long chain fatty acids or salts thereof, and (vi) inorganic fine particles which are added according to necessity, are

described in the first place, and then the toner of the present invention is described.

[0019]

(I) Materials which are used in the present invention:

(i) Toner mother particles:

Toner mother particles contain a binding resin and a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent.

[0020]

(Binding resin)

As binder resins, resins which are ordinarily used as the materials of toners are used. As such resins, polystyrene-based resins, acrylate-based resins or methacrylate-based resins (hereinafter referred to as (meth)acrylate-based resins), styrene-acrylic-based resins, polyester resins, polyethylene resins, epoxy resins, silicone resins, polypropylene resins, fluorine resins, polyamide resins, polyvinyl alcohol resins, polyurethane resins, polyvinyl butyral resins, and copolymers containing the constituents of these resins are used.

[0021]

Among them, polystyrene-based resins and styrene-(meth)acrylate-based resin copolymers are preferably used.

[0022]

As polystyrene resins, e.g., hydrogenated styrene resins, styrene-isobutylene copolymers, acrylonitrile-butadiene-styrene copolymers (ABS resins), acrylonitrile-styrene copolymers (AS resins), acrylonitrile-polyethylene chloride-styrene copolymers (ACS resins), styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-butadiene crosslinked polymers, styrene-butadiene-chlorinated paraffin copolymers, styrene-allyl alcohol copolymers, styrene-butadiene rubbers, styrene-maleic ester copolymers, styrene-isobutylene copolymers, and styrene-maleic anhydride copolymers are exemplified.

[0023]

As styrene-(meth)acrylate-based resin copolymers, e.g., acrylate-styrene-acrylonitrile copolymers (ASA resins), styrene-diethylaminoethyl methacrylate copolymers, styrene-methyl methacrylate copolymers, styrene-n-butyl methacrylate copolymers, styrene-methyl methacrylate-n-butyl acrylate copolymers, styrene-methyl methacrylate-butyl allylate-N-(ethoxymethyl)acrylamide copolymers, styrene-glycidyl methacrylate copolymers, styrene-butadiene-dimethylaminoethyl methacrylate copolymers, styrene-acrylate-maleate copolymers, styrene-methyl methacrylate-2-ethylhexyl acrylate copolymers, styrene-n-butyl allylate-ethyl glycol methacrylate copolymers, styrene-n-butyl methacrylate-acrylic acid copolymers,

styrene-n-butyl methacrylate-maleic anhydride copolymers, styrene-butyl acrylate-isobutylmaleic half ester-divinylbenzene copolymers, styrene-butadiene-acrylate copolymers, and styrene-acrylate copolymers are exemplified.

[0024]

When a toner is fixed by thermal fixation in image formation, the flow softening point (T_m) of a binding resin is preferably low. T_m is preferably from 85 to 140° C, more preferably from 90 to 120°C, and still more preferably from 100 to 110°C. The glass transition temperature (T_g) of a binding resin is preferably from 40 to 90°C, more preferably from 50 to 80°C. A flow softening point (T_m) is measured by using a sample obtained by pressure-molding 1.0 g of a binding resin to make a pellet, with "Flow Tester CFT-500D" (a product of Shimadzu Corporation) on conditions of: heat-up velocity of 5°C/min; cylinder pressure of 2.0 MPa; the hole diameter of a die of 1.0 mm; the hole length of a die of 1.0 mm; and by T_m computing method of a 1/2 method. Further, the glass transition temperature (T_g) of a binding resin is measured by packing 10 mg of a binding resin in an aluminum cell and with "DSC120" (a product of Seiko Instruments Inc.) on conditions of: measuring temperature of from 0 to 200°C; and heat-up velocity of 10°C/min; and the value is read from the DSC curve of the second heat-up time.

[0025]

When a toner is fixed by pressure fixation, wax-like resins are preferably used as the binding resin. Of the above binding resins, polyethylene resins, polyethylene-vinyl acetate copolymers and natural waxes are used as the wax-like resins.

[0026]

The binding resins are manufactured by polymerization, e.g., emulsion polymerization, dispersion polymerization and suspension polymerization, or pulverization including kneading, pulverization and classification processes. Considering the homogeneity and flowability of the finally obtained toner particles, the binding resins obtained by polymerization are preferably used.

[0027]

The binding resins may be used alone or two or more binding resins may be blended. The above-shown binding resins are representative examples and the present invention is not of course limited thereto.

[0028]

(Colorants)

As colorants, the following-shown organic pigments, inorganic pigments and dyes are used. Of organic and inorganic pigments, carbon black, copper oxide, tri-iron tetroxide, manganese dioxide, Aniline Black and active

carbon are used as black pigments.

[0029]

As yellow pigments, chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titan yellow, naples yellow, Naphthol Yellow S, Hansa Yellow, Benzidine Yellow G, Benzidine Yellow GR, Quinoline Yellow Lake, Permanent Yellow NCG, and Tartrazine Lake are used.

[0030]

As orange pigments, red chrome yellow, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G, and Indanthrene Brilliant Orange GKM are used.

[0031]

As red pigments, iron oxide red, cadmium red, red lead, mercury sulfide, cadmium, Permanent Red 4R, Lithol Red, Pyrazolone Red, Watchung Red, calcium salt, Lake Red D, Brilliant Carmine 6B, eosine lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B are used.

[0032]

As violet pigments, manganese violet, Fast Violet B and Methyl Violet Lake are used. As blue pigments, Prussian blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, nonmetal Phthalocyanine Blue, partially chlorinated product of Phthalocyanine Blue, Fast

Sky Blue and Indanthrene Blue BC are used.

[0033]

As green pigments, chrome green, chromium oxide, Pigment Green B, Malachite Green Lake and Final Yellow Green G are used.

[0034]

As white pigments, zinc flower, titanium oxide, antimony white and zinc sulfide are used.

[0035]

As extender pigments, baryta powder, barium carbonate, clay, silica, white carbon, talc and alumina white are used.

[0036]

As dyes, basic dyes, acid dyes, dispersed dyes and direct dyes are used. The examples of such dyes include Nigrosine, Methylene Blue, Rose Bengale, Quinoline Yellow and Ultramarine Blue.

[0037]

When the toner of the present invention is a transparent color toner, the following-shown various pigments and dyes are used as the colorants.

[0038]

As yellow pigments, C.I. 10316 (Naphthol Yellow S), C.I. 11710 (Hansa Yellow 10G), C.I. 11660 (Hansa Yellow 5G), C.I. 11670 (Hansa Yellow 3G), C.I. 11680 (Hansa Yellow G),

C.I. 11730 (Hansa Yellow GR), C.I. 11735 (Hansa Yellow A), C.I. 11740 (Hansa Yellow NR), C.I. 12710 (Hansa Yellow R), C.I. 12720 (Pigment Yellow L), C.I. 21090 (Benzidine Yellow), C.I. 21095 (Benzidine Yellow G), C.I. 21100 (Benzidine Yellow GR), C.I. 20040 (Permanent Yellow NCG), C.I. 21220 (Vulcan Fast Yellow 5) and C.I. 21135 (Vulcan Fast Yellow R) are used.

[0039]

As red pigments, C.I. 12055 (Stirling I), C.I. 12075 (Permanent Orange), C.I. 12175 (Lithol Fast Orange 3GL), C.I. 12305 (Permanent Orange GTR), C.I. 11725 (Hansa Yellow 3R), C.I. 21165 (Vulcan Fast Orange GG), C.I. 21110 (Benzidine Orange G), C.I. 12120 (Permanent Red 4R), C.I. 1270 (Para Red), C.I. 12085 (Fire Red), C.I. 12315 (Brilliant Fast Scarlet), C.I. 12310 (Permanent Red F2R), C.I. 12335 (Permanent Red F4R), C.I. 12440 (Permanent Red FRL), C.I. 12460 (Permanent Red FRLL), C.I. 12420 (Permanent Red F4RH), C.I. 12450 (Light Fast Red Toner B), C.I. 12490 (Permanent Carmine FB), and C.I. 15850 (Brilliant Carmine 6B) are used.

[0040]

As blue pigments, C.I. 74100 (nonmetal Phthalocyanine Blue), C.I. 74160 (Phthalocyanine Blue), and C.I. 74180 (Fast Sky Blue) are used.

[0041]

These colorants may be used alone or a plurality of colorants may be used in combination. The colorants are used in an amount of from 1 to 20 mass% to 100 mass% of the binding resin, preferably from 2 to 10 mass%. When the amount of colorants is more than 20 mass%, the fixing property and transparency of the toner decrease, while when the amount is less than 1 mass%, there is a risk of incapable of obtaining desired image density.

[0042]

(Mold releasing agents)

As the mold releasing agent, paraffin-based waxes, polyolefin-based waxes, modified waxes having an aromatic group, hydrocarbon compounds having an alicyclic group, natural waxes, long chain fatty acids having 12 or more carbon atoms, the esters thereof, metal salts of long chain fatty acids (metal soaps), fatty acid amide and fatty acid bisamide are used. Of the above mold releasing agents, paraffin-based waxes, polyolefin-based waxes and metal soaps are preferably used.

[0043]

The examples of paraffin-based waxes include, e.g., paraffin wax (manufactured by Nippon Oil Co., Ltd. and Nippon Seiro Co., Ltd.), micro-wax (manufactured by Nippon Oil Co., Ltd.), micro-crystalline wax (manufactured by Nippon Seiro Co., Ltd.), hard paraffin wax (manufactured by

Nippon Seiro Co., Ltd.), PE-130 (manufactured by Hoechst A.G.), Mitsui High Wax 110P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 220P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 660P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 210P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 320P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 410P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 420P (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-2130 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-4020 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-5020 (manufactured by Mitsui Petrochemical Industries, Ltd.), beeswax, carnauba wax and montan wax.

[0044]

As polyolefin-based waxes, e.g., low molecular weight polypropylene, low molecular weight polyethylene, oxidation type polypropylene and oxidation type polyethylene are exemplified. The specific examples of polyolefin-based waxes include non-oxidation type

polyethylene waxes, e.g., Hoechst Wax PE520, Hoechst Wax PE130, Hoechst Wax PE190 (manufactured by Hoechst A.G.), Mitsui High Wax 200, Mitsui High Wax 210, Mitsui High Wax 210M, Mitsui High Wax 220, Mitsui High Wax 220M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX 131-P, SANWAX 151-P, and SANWAX 161-P (manufactured by Sanyo Chemical Industries Co., Ltd.), oxidation type polyethylene waxes, e.g., Hoechst Wax PED121, Hoechst Wax PED153, Hoechst Wax PED521, Hoechst Wax PED522, Hoechst Wax Ceridust 3620, Hoechst Wax Ceridust VP130, Hoechst Wax Ceridust VP5905, Hoechst Wax Ceridust VP9615A, Hoechst Wax Ceridust TM9610F, Hoechst Wax Ceridust 3715 (manufactured by Hoechst A.G.), Mitsui High Wax 420M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX E-300 and SANWAX E-250P (manufactured by Sanyo Chemical Industries Co., Ltd.), non-oxidation type polypropylene waxes, e.g., Hoechst Wachs PP230 (manufactured by Hoechst A.G.), and VISCOL 330-P, VISCOL 550-P, VISCOL 660-P (manufactured by Sanyo Chemical Industries Co., Ltd.), and oxidation type polypropylene waxes, e.g., VISCOL TS-200 (manufactured by Sanyo Chemical Industries Co., Ltd.).

[0045]

These mold releasing agents may be used alone or a plurality of compounds may be used in combination. Mold releasing agents having a low softening point (melting

point), e.g., from 40 to 130°C, preferably from 50 to 120°C, are preferably used. A softening point is represented by an endothermic main peak value on the DSC endothermic curve measured with "DSC120" (a product of Seiko Instruments Inc.).

[0046]

As the examples of fatty acid metal salts (metal soaps), e.g., zinc stearate, calcium stearate, magnesium stearate, zinc oleate, zinc palmitate and magnesium palmitate are preferably used.

[0047]

(Dispersants)

Metal soaps and polyethylene glycol and the like are used as the dispersant.

[0048]

(Electrification controlling agents)

A electrification controlling agent is not particularly limited unless it provides a positive charge or a negative charge by friction-charging. An organic electrification controlling agent or an inorganic electrification controlling agent can be used. As the positive electrification controlling agents, commercially available products are used. For example, Nigrosine Base EX (manufactured by Orient Chemical Industry Co., Ltd.), a quaternary ammonium salt P-51 (manufactured by Orient

Chemical Industry Co., Ltd.), Nigrosine Bontoron N-01 (manufactured by Orient Chemical Industry Co., Ltd.), Sudan Chief Schwarz BB (Solvent Black 3: Color Index 26150), Fetschwarz HBN (C.I. No. 26150), Brilliant Spirits Schwarz TN (manufactured by Farbenfabriken Bayer A.G.), and Zaponschwarz X (manufactured by Farberke Hoechst A.G.) are exemplified. Of these products, a quaternary ammonium salt P-51 is preferably used. In addition to the above products, alkoxyated amine, alkylamide and chelate pigments of molybdic acids are also used as a positive electrification controlling agent. These positive electrification controlling agents may be used alone or a plurality of compounds may be used in combination.

[0049]

As negative electrification controlling agents, a commercially available negative electrification controlling agents can be used. For example, Oil Black (Color Index 26150), Oil Black BY (manufactured by Orient Chemical Industry Co., Ltd.), Bontron S-22 (manufactured by Orient Chemical Industry Co., Ltd.), salicylic acid metal complex E-81 (manufactured by Orient Chemical Industry Co., Ltd.), thioindigo series pigments, sulfonylamine derivatives of copper phthalocyanine, Spiron Black TRH (manufactured by HODOGAYA CHEMICAL Co., Ltd.), Bontoron S-34 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine SO

(manufactured by Orient Chemical Industry Co., Ltd.), Celesschwarz (R)G (manufactured by Farbenfabriken Bayer A.G.), Chromogeneschwarz ETOO (C.I. No. 14645), and Azo Oil Black (R) (manufactured by National Aniline Co.). Of these products, salicylic acid metal complex E-81 is preferably used. These negative electrification controlling agents can be used alone or a plurality of compounds may be used in combination.

[0050]

(Magnetic agents)

As magnetic agents, metallic powders of, e.g., Fe, Co, Ni, Cr, Mn and Zn, metallic oxides, e.g., Fe_3O_4 , Fe_2O_3 , Cr_2O_3 , ferrite, and alloys showing ferromagnetism by thermal treatment, e.g., alloys containing manganese and acid, are exemplified. These magnetic agents may be subjected to treatment in advance with a coupling agent.

[0051]

(Manufacture of toner mother particles)

Toner mother particles are manufactured by adding a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent, to a binding resin. A method of manufacturing mother particles by a pulverizing method including kneading, pulverization and classification processes is described below. Firstly, a binding agent, a

colorant and additives, e.g., a mold releasing agent, in prescribed amounts are introduced into a mixer, e.g., Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED) and blended homogeneously. The blending ratios of additives, e.g., a binding resin, a colorant, an electrification controlling agent, and a mold releasing agent, are decided arbitrarily taking the color and electrification property of the toner into consideration.

[0052]

The above mixture is then introduced into a twin-screw kneading extruder (PCM-30, manufactured by IKEGAI KASEI CO., LTD) and homogeneously melt kneaded. As the melt-kneading means besides the above, continuous kneaders, e.g., "TEM-37" (manufactured by TOSHIBA MACHINE CO., LTD.) and "KRC Kneader" (manufactured by KURIMOTO, LTD.), and batch type kneaders, e.g., a hot-pressing kneader, are exemplified. Toner mother particles having a desired average particle size can be obtained by pulverizing the obtained melt-kneaded product by means of a grinding means. Pulverization is performed by, e.g., impinging pulverization by jet air using a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION) or IDS-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), in addition, by a mechanical pulverizer Turbo Mill (a product of Kawasaki Heavy Industries, Ltd.) or Super Rotor (a product of

Nisshin Engineering), etc.

[0053]

In the next place, the particle size of the obtained toner mother particles is adjusted by wind power or rotation of rotors. For instance, a sharp particle size distribution can be obtained by using, e.g., a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), DSX-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), or Elbow-Jet (a product of NITTETSU MINING CO., LTD.).

[0054]

Toner mother particles may also be manufactured by a method of dissolving internal additives constituting the toner mother particles, e.g., a resin and a colorant, in an organic solvent, dispersing and granulating the aqueous solvent with a classifying agent and an emulsifying agent, and then separating and drying the emulsion.

[0055]

(ii) Negatively electrifiable silica fine particles:

Negatively electrifiable silica fine particles which are used in the present invention are not particularly restricted. Negatively electrifiable silica fine particles having an average particle size of from 4 to 120 nm, preferably from 5 to 50 nm, and more preferably from 10 to 40 nm are generally used. The smaller the average particle

size of negatively electrifiable silica fine particles, the higher is the flowability of the toner obtained. When the average particle size is smaller than 4 nm, the negatively electrifiable silica fine particles are liable to be buried in the toner mother particles. When the average particle size is larger than 120 nm, there is the possibility of conspicuous degradation of the flowability. In the specification of the invention, the terminology "average particle size" of the fine particles of negatively electrifiable silica, positively electrifiable silica, toner mother particles and toner particles means a volume average particle size, unless otherwise indicated.

[0056]

It is preferred that negatively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of negatively electrifiable silica fine particles hydrophobic, the flowability and electrification property of the toner are further improved. The hydrophobitization treatment of silica fine particles is carried out according to wet methods or dry methods usually used in the industry with a silane compound, e.g., aminosilane, hexmethyldisilazane, or dimethyldicyclosilane; or a silicone oil, e.g., dimethylsilicone, methylphenylsilicone, fluorine-modified silicone oil,

alkyl-modified silicone oil, amino-modified silicone oil, or epoxy-modified silicone oil.

[0057]

As negatively electrifiable hydrophobic silica fine particles, commercially available RX200 and RX50 (manufactured by Nippon Aerosil Co., Ltd.) and TG811F, TG810G and TG308F (manufactured by Cabot) are used.

[0058]

(iii) Positively electrifiable silica fine particles:

Positively electrifiable silica fine particles which are used in the present invention are not especially limited. The volume average particle size of positively electrifiable silica fine particles is preferably from 10 to 50 nm, more preferably from 15 to 40 nm, taking the flowability and the like into consideration.

[0059]

It is preferred that positively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of positively electrifiable silica fine particles hydrophobic, the flowability and chargeability of the toner can be improved. The hydrophobitization of positively electrifiable silica fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0060]

As positively electrifiable hydrophobic silica fine particles, commercially available NA50H (manufactured by Nippon Aerosil Co., Ltd.) and TG820F (manufactured by Cabot) are used.

[0061]

(iv) Titanium oxide (titania) fine particles:

Titanium oxide fine particles for use in the present invention are not particularly limited. Titanium oxide fine particles having a relatively small electrical resistivity are preferably used. Titanium oxide may take a crystal form of rutile type, anatase type, rutile-anatase type. Titanium oxide of any crystal form may be used, but titanium oxide of a rutile-anatase type is preferably used for the reason that the adjustment of electric charge is easy and a rutile-anatase type titanium oxide is difficult to be buried in toner mother particles even when the number of sheets of printing increases.

[0062]

The size of titanium oxide fine particles is not particularly restricted but it is preferred that the particle size or long axis length be 10 to 30 nm. In the case of a rutile-anatase type titanium oxide, titanium oxide fine particles having a long axis length of about 20 nm are preferred.

[0063]

By making the surfaces of titanium oxide fine particles hydrophobic, a stable electrification property can be maintained, and the flowability of the toner can be improved. The hydrophobitization of titanium oxide fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0064]

As hydrophobic titanium oxide fine particles, STT-30s (manufactured by TITAN KOGYO KABUSHIKI KAISHA) and the like are used.

[0065]

(v) Long chain fatty acid or salt thereof

The long chain fatty acids or salts thereof for use in the present invention are not particularly restricted. As the long chain fatty acids, long chain fatty acids preferably having from 10 to 30 carbon atoms, more preferably from 12 to 28 are used. As the long chain fatty acids, long chain saturated fatty acids and long chain unsaturated fatty acids are exemplified. Long chain saturated fatty acids are preferably used. The long chain fatty acids may be branched, but long chain saturated fatty acids, e.g., stearic acid, is preferably used.

[0066]

It is preferred to use the long chain fatty acids in the form of salts, and more preferably in the form of metal salts (so-called metal soaps). The metal salts of the long chain fatty acids are not particularly restricted and, e.g., calcium salts, zinc salts, magnesium salts, aluminum salts and lithium salts are exemplified. As the metal soaps, e.g., magnesium stearate, calcium stearate and zinc stearate are exemplified, and fine particles of these metal soaps are preferably used. Particles comprising long chain saturated fatty acids or salts thereof may be used alone or as mixtures of two or more kinds.

[0067]

(vi) Inorganic fine particles

Inorganic fine particles other than titanium oxide fine particles are also externally added for the purpose of controlling the electrification property and improving flowability. For instance, as inorganic fine particles, fine particles of metallic oxide, e.g., aluminum oxide, strontium oxide, tin oxide, zirconia oxide, magnesium oxide, and indium oxide; fine particles of nitrides, e.g., silicon nitride; fine particles of carbides, e.g., silicon carbide; fine particles of metal salts, e.g., calcium sulfate, barium sulfate and calcium carbonate; and inorganic fine particles of these are exemplified. Fine particles of metallic oxides having a relatively small electrical

resistivity, e.g., $10^9\Omega\text{-cm}$ or less are preferably used.

[0068]

The sizes of inorganic fine particles added are not particularly restricted, but the sizes of from 10 to 30 nm are preferred. It is preferred that the surfaces of these inorganic fine particles be subjected to hydrophobitization treatment for the purpose of improving the stabilization of electrification characteristics. The hydrophobitization treatment of inorganic fine particles is performed by the same method as used in the hydrophobitization treatment of negatively electrifiable silica fine particles or positively electrifiable silica fine particles.

[0069]

(II) Toner of the present invention and manufacturing method:

In the present invention, three kinds of toners (toner A, toner B and toner C) are manufactured by specifying the addition order of additives.

[0070]

[Toner A]

Toner A can be obtained by performing in the order of (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; (2) a process of externally adding titanium oxide fine particles,

and (3) a process of externally adding positively electrifiable silica fine particles.

[0071]

A method of manufacturing the toner A of the present invention is described in further detail below. In process (1), negatively electrifiable silica fine particles are externally added to toner mother particles containing a binding resin and a colorant. In process (1), negatively electrifiable silica fine particles having a uniform average particle size may be used alone, but it is preferred to use two or more negatively electrifiable silica fine particles respectively having different average particle sizes in combination. In general, negatively electrifiable silica fine particles having a small average particle size (small particle size silica) are used, but when negatively electrifiable silica fine particles having a large average particle size (large particle size silica) are used in combination with small particle size silica, not only the absolute value of the quantity of electrification can be made great, but small particle size silica can be prevented from being buried in toner mother particles due to the resistance of large particle size silica, as compared with the case where small particle size silica is used alone, so that the stability of electrification of the toner can be ensured for a long

period of time. Further, it becomes possible to improve the flowability of the toner, and improve the storage stability of the toner by the blocking effect against heat. It is preferred to use negatively electrifiable silica fine particles having an average particle size of from 5 to 20 nm, preferably from 10 to 15 nm, as the small particle size silica and negatively electrifiable silica fine particles having an average particle size of from 20 to 50 nm, preferably from 20 to 40 nm, as the large particle size silica. In addition, the difference in average particle size between large particle size silica and small particle size silica is preferably 10 nm or more, and more preferably 20 nm or more.

[0072]

For the purpose of imparting flowability to a toner and ensuring the stability of electrification for a long period of time, the addition ratio of large particle size silica to small particle size silica in a mass ratio is from 1/3 to 3/1, preferably from 1/2 to 2/1, and more preferably from 1/1.5 to 1.5/1.

[0073]

Large particle size silica and small particle size silica may be blended at the same time, alternatively either silica particles may be added prior to the other.

[0074]

In the next place, titanium oxide fine particles are externally added (process (2)), and then positively electrifiable silica fine particles are externally added (process (3)). It is preferred that the surfaces of titanium oxide fine particles and positively electrifiable silica fine particles should be subjected to hydrophobitization treatment. By making the surfaces of titanium oxide fine particles and positively electrifiable silica fine particles hydrophobic, the flowability of the toner can be improved.

[0075]

The addition amounts of negatively electrifiable silica fine particles, titanium oxide fine particles and positively electrifiable silica fine particles which are used in the manufacture of toner A in the present invention are variable according to the particle size distribution or flowability of toner mother particles, or the particle size distribution of external additives, and a desired quantity of electrification. In the case of negatively electrifiable silica fine particles, e.g., the above small particle size silica is added in an amount of from 0.5 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably 0.7 to 1.5 mass parts. In the case of large particle size silica, the addition amount is from 0.5 to 2.0 mass parts to 100 mass parts of the toner

mother particles, and preferably from 0.6 to 1.5 mass parts. When large particle size silica and small particle size silica are used in combination, they are added in total amount of from 0.5 to 2.5 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.7 to 2.0 mass parts, taking the above-described blending ratio into consideration.

[0076]

Titanium oxide fine particles are added in an amount of from 0.2 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.3 to 1.5 mass parts.

[0077]

Positively electrifiable silica fine particles are added in an amount of from 0.1 to 1.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.2 to 0.8 mass parts.

[0078]

It is preferred that titanium oxide fine particles and positively electrifiable silica fine particles be externally added in a mass ratio of 1/3 to 3/1 from the point that the electric charge can be adjusted without bringing about an extreme reduction of electric resistance of the toner.

[0079]

If necessary, (vi) inorganic fine particles may be added for the purpose of the adjustment of electric charge and the improvement of flowability. The inorganic fine particles may be added before or after process (2) and process (3), or during process (2) or process (3), provided that they are added after the external addition of negatively electrifiable silica fine particles (process (1)). It is preferred to add inorganic fine particles simultaneously with the addition of titanium oxide fine particles in process (2) from the viewpoint of the stabilization of the electrification property.

[0080]

External addition of negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles to toner mother particles is carried out by machines or methods usually used in this industry, e.g., high speed fluid mixers, such as a Henschel mixer or Perpenmyer, and mixers using a mechanochemical method. Toner A can be obtained, for example, by putting toner mother particles and negatively electrifiable silica fine particles into a Henschel mixer and stirring at a prescribed stirring velocity for prescribed time, introducing titanium oxide fine particles and further stirring at a prescribed stirring velocity for prescribed time, and finally

introducing positively electrifiable silica fine particles and stirring at a prescribed stirring velocity for prescribed time. The velocity and time of stirring in each process can be set independently, but the conditions may be the same.

[0081]

According to the manufacturing method of toner A of the present invention, since the static attraction between toner mother particles and negatively electrifiable silica fine particles is not hindered by adding negatively electrifiable silica fine particles alone in the first place in process (1), and the difference between the work function of negatively electrifiable silica fine particles and the work function of toner mother particles is large, negatively electrifiable silica fine particles can be strongly adhered to toner mother particles. Therefore, the desorption of negatively electrifiable silica fine particles is prevented and the fluctuation of electrification property lessens, as a result, an electrification property can be stabilized for a long period of time.

[0082]

In process (2), as compared with the case where titanium oxide fine particles are added simultaneously with negatively electrifiable silica fine particles or

positively electrifiable silica fine particles, from the relationship between the work function of titanium oxide fine particles and the work function of mother particles having been externally added therein negatively electrifiable silica fine particles, the liberation of titanium oxide fine particles can be restrained.

[0083]

Titanium oxide fine particles have low electrical resistance, accordingly there is high possibility that the electric charge is excessively lost when titanium oxide fine particles are present on the surface of the toner. On the other hand, positively electrifiable silica fine particles are positively electrified and have a high electrical resistance value. Therefore, by externally adding positively electrifiable silica fine particles in process (3) after titanium oxide fine particles have been added, the positively electrifiable silica fine particles function as the electric charge adjuster and the reduction of the electric resistivity of the toner is restrained, thereby the electric charge is unified. Further, since positively electrified toner particles come to be liberated and present in the toner in an appropriate rate, the flowability of the toner becomes good and, at the same time, the liberated positively electrified toner particles function as the carrier, so that the electrification

property becomes more uniform.

[0084]

On the other hand, conventional toners, e.g., the toners disclosed in patent literature 1 to 4, are toners obtained by externally adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles at the same time, and it is thought that by adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles at the same time, the static attraction between the toner mother particles and the negatively electrifiable silica fine particles becomes small, and the desorption of the negatively electrifiable silica fine particles are liable to occur.

[0085]

As described above, as compared with conventional toners obtained by the simultaneous mixture, the toner of the present invention has a uniform electrification property, and has excellent effects such that a uniform electrification property and excellent flowability are stably maintained for a long period of time by restraining the liberation of negatively electrifiable and/or positively electrifiable silica fine particles or titanium oxide fine particles.

[0086]

[Toner B]

Toner B can be obtained by performing in the order of (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant, (2) a process of externally adding titanium oxide fine particles, (3) a process of externally adding positively electrifiable silica fine particles, and (4) a process of externally adding particles comprising a long chain fatty acid or a salt thereof. Processes (1) to (3) in the manufacturing process of toner B are in common with processes (1) to (3) in the manufacturing process of toner A, and materials and external addition methods used in these processes are also in common with those in the case of toner A. Further, the fact that external addition of large particle size silica and small particle size silica as mixture in the above specific range is preferred is also in common with the case of the manufacture of toner A. Toner B can be obtained by performing (4) a process of externally adding particles comprising a long chain fatty acid or a salt thereof after process (3). By further externally adding particles comprising a long chain fatty acid or a salt thereof after process (3), the liberation of positively electrifiable silica fine particles and titanium oxide fine particles can be restrained, and the stability of electrification is

further improved.

[0087]

As described above, particles comprising a long chain fatty acid or a salt thereof can restrain the liberation of positively electrifiable silica fine particles and titanium oxide fine particles. This is probably because particles comprising a long chain fatty acid or a salt thereof function as the binding agent of positively electrifiable silica fine particles and titanium oxide fine particles, but it is also thought that particles comprising a long chain fatty acid or a salt thereof function as the coagulation inhibitor, auxiliary flowing agent and lubricant.

[0088]

Particles comprising a long chain fatty acid or a salt thereof are added in an amount of from 0.1 to 1.0 mass part to 100 mass parts of toner mother particles, preferably from 0.1 to 0.5 mass part. The method of external addition of particles comprising a long chain fatty acid or a salt thereof is not particularly limited and the external addition methods of toner A are applied.

[0089]

The thus-obtained toner B has uniform electrification property as compared with toners obtained by conventional simultaneous blending methods, and this

electrification property is stably maintained for a long period of time, and excellent flowability is maintained for a long period of time. As compared with toner A, toner B has excellent advantage such that the electrification property is further improved.

[0090]

[Toner C]

Toner C can be obtained by performing in the order of (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant, (2) a process of externally adding titanium oxide fine particles, and (3') a process of externally adding positively electrifiable silica fine particles, and particles comprising a long chain fatty acid or a salt thereof.

[0091]

Processes (1) and (2) in the manufacturing process of toner C are in common with processes (1) and (2) in the manufacturing process of toner A and toner B. However, toner C is different from toner A and toner B in the point: in toner A, only positively electrifiable silica fine particles are added in process (3), in toner B, positively electrifiable silica fine particles are added in process (3) and particles comprising a long chain fatty acid or a salt thereof are added separately in process (4) in this

order. Contrary to this, in toner C, positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof are simultaneously added in step (3').

[0092]

Toner C obtained by processes (1) to (3') has various advantages including the effects of process (1) that the desorption of negatively electrifiable silica fine particles can be prevented, the fluctuation of electrification property lessens, and the electrification property can be maintained stably for a long period of time, the effect of process (2) that the liberation of titanium oxide fine particles can be restrained from the relationship with the work function of mother particles having added thereto negatively electrifiable silica fine particles, in addition, the effect of process (3') that the liberation of silica fine particles and titanium oxide fine particles can further be inhibited, and electrification can be further stabilized.

[0093]

In externally adding negatively electrifiable silica fine particles in process (1), that the external addition of large particle size silica and small particle size silica as mixture in the above specific range is preferred is the same as in the case of toner A. Further, the

addition amounts of negatively electrifiable silica fine particles, positively electrifiable silica fine particles, and titanium oxide fine particles in toner C, and the external addition methods of these external additives are the same as those in the case of toner A. Further, when inorganic fine particles are added according to necessity, it is preferred that the inorganic fine particles are added simultaneously with the external addition of titanium oxide fine particles in process (2), or between process (2) and process (3').

[0094]

The toners A, B and C of the invention can be used in any type of image-forming apparatus, e.g., image-forming apparatus using one-component series toners, or image-forming apparatus using two-component series toners, may be used. Image-forming apparatus of a contact development system or image-forming apparatus of a non-contact development system may also be used. Image-forming apparatus of a contact development system using one-component series toners capable of using the toner of the invention are described in detail, e.g., in patent literature 13. The image-forming apparatus of the present invention is equipped with at least a latent image carrier on which an electrostatic latent image is formed represented by a photosensitive material; a toner carrier

for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier represented by a developing roller; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier. The toner of the present invention is held in a toner holder, carried from the toner holder to the developing roller (the toner carrier) and supplied to the photosensitive material (the latent image carrier) via the developing roller (the toner carrier), transferred, thereby an image is formed. The toner regulating member adjusts the amount of the toner so that an excess amount of the toner is not supplied to the photosensitive material (the latent image carrier) from the developing roller (the toner carrier).

[0095]

[Example]

The present invention is illustrated with reference to examples below.

[0096]

(Preparation of toner mother particles)

One hundred (100) mass parts of a styrene-acrylic-based binding resin, 3.5 mass parts of a red pigment (C.I. 12055), and 1.0 mass part of chromium salicylate complex were put into Henschel Mixer 20B (a product of MITSUI

MINING COMPANY, LIMITED), and homogeneously blended. The mixture was melt-kneaded with a two-shaft kneading extruder PCM-30 (manufactured by IKEGAI KASEI CO., LTD), and after cooling, pulverized by jet air with a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION). The pulverized product was classified with a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), to thereby prepare toner mother particles having a volume average particle size of 8.5 μm .

[0097]

(External additives)

The external additives externally added to toner mother particles in Examples are shown in Table 1 below.

[0098]

Table 1

| | External Additive | Trade Name | Average Particle Size | Manufacturer |
|----|---------------------------------|--|-----------------------|------------------------------|
| a1 | Negatively electrifiable silica | Negatively electrifiable hydrophobic silica RX200 | 15 nm | Nippon Aerosil Co., Ltd. |
| a2 | Negatively electrifiable silica | Negatively electrifiable hydrophobic silica RX50 | 40 nm | Nippon Aerosil Co., Ltd. |
| b | Titanium oxide | Hydrophobic titanium oxide*) STT-30S | Long axis: 20 nm | TITAN KOGYO KABUSHIKI KAISHA |
| c | Positively electrifiable silica | Positively electrifiable hydrophobic silica NA50H | 30 nm | Nippon Aerosil Co., Ltd. |
| d | Long chain fatty acid salt | Magnesium stearate | | |

*) Rutile-anatase type

[0099]

(External addition process)

In Examples of the invention, external addition process in each process was performed by adding prescribed amounts of external additives to 100 mass parts of toner mother particles, and stirring the constituents by using a Henschel Mixer FM20B (a product of MITSUI MINING COMPANY, LIMITED) for 3 minutes with ZOSO type stirring blades at 2,000 rpm. For example, in manufacturing process (2) of toner A, a prescribed amount of titanium oxide fine particles to 100 mass parts of the toner mother particles were added to the mixture obtained in process (1) and the mixture was subjected to stirring process with a Henschel Mixer FM20B on the same condition as above.

[0100]

(EXAMPLE 1: Preparation of toner A)

External addition process was performed by adding 1 mass part of RX200 to 100 mass parts of the above-obtained toner mother particles (process (1)). External addition process was performed by adding 0.5 mass part of STT-30S to the mixture obtained in process (1) (process (2)). Subsequently, external addition process was performed by adding 0.5 mass part of NA50H to the mixture obtained in process (2) (process (3)), thereby toner A was obtained. The process is described in Table 2 below.

[0101]

(EXAMPLE 2: Preparation of toner B)

Toner B was prepared by external addition of further adding 0.1 mass part of magnesium stearate powder to toner A obtained in Example 1. The process is described in Table 2 below.

[0102]

(EXAMPLE 3: Preparation of toner C1)

External addition process was performed by adding 1 mass part of RX200 to 100 mass parts of the toner mother particles (process (1)). External addition process was performed by adding 0.5 mass part of STT-30S to the mixture obtained in process (1) (process (2)). Subsequently, external addition process was performed by adding 0.5 mass parts of NA50H and 0.1 mass part of magnesium stearate to the toner obtained in process (2) (process (3)), thereby toner C1 was prepared. The process is described in Table 2 below.

[0103]

(EXAMPLE 4: Preparation of toner C2)

Toner C2 was prepared in the same manner as in Example 3 by external addition process, except for adding 0.5 mass part of RX200 and 0.5 mass part of RX50 in place of adding 1 mass part of RX200 in process (1). The process is described in Table 2 below.

[0104]

(COMPARATIVE EXAMPLE 1)

Toner D of Comparative Example 1 was prepared in the same manner as in Example 1, except that external addition process by blending negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles in the same proportion as in Example 1 was performed at a time. The process is described in Table 2 below.

[0105]

(COMPARATIVE EXAMPLE 2)

Toner E of Comparative Example 2 was prepared by the same external addition process as in Example 1, except that the order of process (2) and process (3) was replaced, i.e., positively electrifiable silica fine particles were added after negatively electrifiable silica fine particles, and then titanium oxide fine particles were added. The process is described in Table 2 below.

[0106]

(COMPARATIVE EXAMPLE 3)

Toner F of Comparative Example 3 was prepared by the same external addition process as in Example 1, except for omitting process (3) (positively electrifiable silica fine particles were added). The process is described in Table 2 below.

[0107]

(COMPARATIVE EXAMPLE 4)

Toner G of Comparative Example 4 was prepared in the same manner as in Example 2, except that external addition process by blending negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles in the same proportion as in Example 2 was performed at a time. The process is described in Table 2 below.

[0108]

Table 2

| | External Additives | | | | | Order of External Addition | | | | |
|-----------------------|--------------------|-----|-----|-----|-----|----------------------------|--------------|-------------|--------------|----------|
| | a1 | a2 | b | c | d | First Stage | Second Stage | Third Stage | Fourth Stage | |
| Example 1 | 1.0 | - | 0.5 | 0.5 | - | a1 | b | c | - | Toner A |
| Example 2 | 1.0 | - | 0.5 | 0.5 | 0.1 | a1 | b | c | d | Toner B |
| Example 3 | 1.0 | - | 0.5 | 0.5 | 0.1 | a1 | b | c+d | - | Toner C1 |
| Example 4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.1 | a1+a2 | b | c+d | - | Toner C2 |
| Comparative Example 1 | 1.0 | - | 0.5 | 0.5 | - | a1+b+c | - | - | - | Toner D |
| Comparative Example 2 | 1.0 | - | 0.5 | 0.5 | - | a1 | c | b | - | Toner E |
| Comparative Example 3 | 1.0 | - | 0.5 | - | - | a1 | b | - | - | Toner F |
| Comparative Example 4 | 1.0 | - | 0.5 | 0.5 | 0.1 | a1+b+c+d | - | - | - | Toner G |

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0109]

(EXAMPLE 5)

Toners A to G obtained by the above methods (Table 2) were evaluated. Items and methods of evaluations are as follows.

[0110]

1. Liberation rate of external additives (silica fine particles, titanium oxide fine particles):

The liberation rate of external additives (silica fine particles and titanium oxide fine particles) was measured with PT1000 Particle Analyzer (a product of Yokogawa Electric Corporation). The details of measuring method of the liberation rate of external additives are disclosed in patent literature 7 (JP-A-2002-202622). Describing the principle in brief, liberation rate is obtained by introducing toner particles into plasma, exciting the toner particle to emit light, and measuring the intensity and time of the emission. For example, toner particles to which external additive SiO_2 has been added are introduced into plasma, and the emission intensity of SiO_2 in the toner particles is measured. Assuming that the toner particle to which SiO_2 has been externally added is a spherical particle, the particle size of the spherical particle (equivalent particle size) is obtained from the emission intensity. Similarly to the case of the toner

particle, the equivalent particle size of the liberated SiO_2 can be obtained from the emission intensity. However, since the emission intensity of the liberated SiO_2 is small, the equivalent particle size is small. Accordingly, the liberated external additive can be distinguished from the toner particles by comparing equivalent particle sizes. Therefore, the liberation rate of SiO_2 can be obtained according to the following equation (X), by obtaining all the detected number of external additive SiO_2 , and taking the number of individuals having smaller equivalent particle size as the number of particles of the liberated external additive.

[0111]

[mathematical formula 1]

Liberation rate = (detected number of liberated external additive/all detected number of external additive) x 100 (%) (X)

[0112]

Whether SiO_2 is adhered to a toner particle or liberated is distinguished by making use of the fact that SiO_2 adhered to a toner particle emits light synchronously with the toner particle, but SiO_2 which is not adhered to a toner particle does not radiate synchronously with the toner particle and the time of emission deviates from that of the toner particle (asynchronously). On the basis of

the measured value, the liberation rate can be obtained by the following equation (Y).

[0113]

[mathematical formula 2]

Liberation rate = (asynchronous count of external additive/asynchronous count + synchronous count of external additive) x 100 (%) (Y)

[0114]

A method represented by equation (Y) was adopted in the present invention. In addition, the measurement of the liberation rate of titanium oxide fine particles is performed in the same manner as above by exciting titanium oxide fine particles to emit light in plasma. The volume average particle size of toner mother particles can also be obtained, e.g., by making a colorant contained in the toner mother particles emit light in plasma, and obtaining the equivalent particle size.

[0115]

2. Uniformity of quantity of electrification and electrification:

The quantity of electrification of a toner is measured as follows with E-SPART Analyzer (manufactured by HOSOKAWA MICRON CORPORATION). Each of the toners prepared in Examples 1-4 and Comparative Examples 1-4 and carrier were mixed and stirred, to thereby electrify the toner.

Nitrogen gas was then blown to the mixture of the toner and the carrier to separate the toner and the carrier. In the next place, the quantity of electrification of every toner (Q/m) was measured, and the distribution of the quantities of electrification of the toners was obtained. The uniformity of electrification is judged as follows. In number distribution of the quantity of electrification of every one toner (Q/m), the difference between the quantity of electrification of the maximum frequency (Q_1/m_1) and the value obtained by dividing the total quantity of electrification of the measured toners by the measured count (the number) (Q_2/m_2), i.e., the smaller the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the sharper is the distribution of the quantity of electrification (uniform), and the greater the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the broader is the distribution of the quantity of electrification (nonuniform).

[0116]

As the carrier, KBN100 ferrite carrier (manufactured by Hitachi Metals, Ltd.) was used.

[0117]

3. Electrical resistivity of toner:

Electrical resistivity was measured with a hybrid type electrical resistivity tester model DRT-1 (manufactured by Sankyo Biotics according to JIS B9915).

[0118]

The results of the above evaluation are shown in
Table 3 below.

[0119]

Table 3

| | | a | | b | c | | Electrical Resistivity (Ω·cm) | Liberation Rate of Silica (%) | Liberation Rate of Titanium Oxide (%) |
|-----------------------|----------|---------------------------------------|---------------------------------------|---|------------|--|-------------------------------|-------------------------------|---------------------------------------|
| | | Q ₁ /m ₁ (μC/g) | Q ₂ /m ₂ (μC/g) | | a-b (μC/g) | | | | |
| Example 1 | Toner A | -12.48 | -15.69 | | 3.21 | | 4.2x10 ¹⁶ | 0.43 | 0.68 |
| Example 2 | Toner B | -11.86 | -12.26 | | 0.40 | | 4.3x10 ¹⁶ | 0.38 | 0.46 |
| Example 3 | Toner C1 | -11.53 | -11.66 | | 0.13 | | 4.4x10 ¹⁶ | 0.38 | 0.51 |
| Example 4 | Toner C2 | -11.56 | -11.69 | | 0.13 | | 4.1x10 ¹⁶ | 0.39 | 0.43 |
| Comparative Example 1 | Toner D | -13.56 | -19.63 | | 6.07 | | 4.6x10 ¹⁶ | 0.89 | 1.06 |
| Comparative Example 2 | Toner E | -12.96 | -16.31 | | 3.35 | | 4.5x10 ¹⁶ | 0.46 | 1.28 |
| Comparative Example 3 | Toner F | -13.44 | -20.68 | | 7.24 | | 7.9x10 ¹⁵ | 0.38 | 0.98 |
| Comparative Example 4 | Toner G | -12.96 | -16.31 | | 3.35 | | 4.5x10 ¹⁶ | 0.46 | 1.28 |

[0120]

From the results of column c in Table 3, it can be seen that the toners obtained by the external addition of negatively electrifiable silica fine particles, titanium oxide fine particles, positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof in the specific order are excellent in the uniformity of electrification, low in the liberation rate of silica fine particles, and also very low in the liberation rate of titanium oxide fine particles, as compared with the case where these external additives are added at the same time (Comparative Examples 1 and 4), the case where titanium oxide fine particles and positively electrifiable silica fine particles are added in the reverse order (Comparative Example 2), and the case where positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof are not externally added.

[0121]

In Example 1 and Comparative Example 1, negatively electrifiable silica fine particles, titanium oxide fine particles and positively electrifiable silica fine particles are used in the same amounts respectively. However, it is suggested by the results of the liberation rates of silica that strong adhesion of negatively

electrifiable silica fine particles is brought about by changing the methods of external addition.

[0122]

Further, it can be seen from the comparison of Example 1 and Comparative Example 2 that the liberation rate of titanium oxide fine particles greatly reduces by the external addition in the order of titanium oxide fine particles - positively electrifiable silica fine particles (Example 1) in place of the order of positively electrifiable silica fine particles - titanium oxide fine particles (Comparative Example 2).

[0123]

It is seen from the comparison of the results in Example 1 and Comparative Example 3 that the electrical resistance of a toner does not extremely reduce even when titanium oxide fine particles and positively electrifiable silica fine particles are used in combination and the adjustment of electric charge is possible. When titanium oxide fine particles are present on the surface of a toner, the electric charge is liable to be lost excessively easily, since the electrical resistance value is small, but the excess vanishing of electric charge can be prevented and the electric charge of the toner at large can be adjusted to a lower level and uniform by performing external addition in the order of titanium oxide fine particles -

positively electrifiable silica fine particles.

[0124]

From the comparison of the results in Examples 2 to 4 and in Comparative Example 4, it can be seen that the amount of liberated silica fine particles and titanium oxide fine particles lowers (in other words, the silica fine particles are efficiently taken in the toner mother particles) by adding a metal salt of a long chain fatty acid (magnesium stearate) after the external addition of positively electrifiable silica fine particles or at the same time with positively electrifiable silica fine particles. By this fact, it becomes possible to lessen the aging fluctuation of electric charge at use time.

[0125]

Of these toners, since the toners of Examples 3 and 4 show a uniform electrification property, and the liberation rate of the titanium oxide fine particles of the toner of Example 4 is small, it is thought that the electrification is maintained uniform also at use time.

[0126]

(EXAMPLE 6)

A copier (model LP-9300 manufactured by Seiko Epson Corporation) was charged with the toner obtained in Example 4, and printing of 3,000 sheets was performed. Printing was begun when 5% of the toner was consumed, and properties

of the toner before and after printing were compared. The results obtained are shown in Table 4 below. The results of toner C1 obtained in Example 3 wherein negatively electrifiable silica a1 and a2 are not used in combination, and the results of toner G obtained in Comparative Example 4 are also shown in Table 4 for comparison.

[0127]

Table 4

| | | a | b | c | Electrical Resistivity ($\Omega \cdot \text{cm}$) | Liberation Rate of Silica (%) | Liberation Rate of Titanium Oxide (%) |
|-------------------------------------|--------------------------------|----------------------------------|----------------------------------|----------------------------|--|-------------------------------|---------------------------------------|
| | | Q_1/m_1 ($\mu\text{C/g}$) | Q_2/m_2 ($\mu\text{C/g}$) | a-b ($\mu\text{C/g}$) | | | |
| Example 4 Toner C2 | Initial stage | -11.56 | -11.69 | 0.13 | 4.1×10^{16} | 0.39 | 0.43 |
| | After printing 3,000 sheets | -12.79 | -13.56 | 0.77 | 4.3×10^{16} | 0.38 | 0.63 |
| Example 3 Toner C1 | Initial stage | -11.53 | -11.66 | 0.13 | 4.4×10^{16} | 0.38 | 0.51 |
| | After printing 3,000 sheets | -15.29 | -17.81 | 2.52 | 5.3×10^{16} | 0.42 | 0.69 |
| Comparative Example 4 Toner G | Initial stage | -12.96 | -16.31 | 3.35 | 4.5×10^{16} | 0.46 | 1.28 |
| | After printing 3,000 sheets | -14.81 | -19.63 | 4.82 | 6.2×10^{16} | 0.49 | 1.58 |

[0128]

The toners of Examples 3 and 4 are greatly improved in the point of the liberation rates of silica and titanium oxide as compared with the toner of Comparative Example 4. From the comparison of the toners in Examples 3 and 4, it can be seen that the liberation rate of the titanium oxide fine particles after printing 3,000 sheets is small in both toners and uniform electrification properties are maintained, in particular the increase in the liberation rate in toner C2 obtained in Example 4 wherein negatively electrifiable silica a1 and a2 are used in combination is less than the increase in the liberation rate in toner C1 in Example 3 wherein a1 and a2 are not used in combination. This fact shows that the fluctuation of the quantity of electrification, the electric resistivity, and the liberation of silica and titanium oxide of a toner with the increase of the number of sheets of printing can be restrained by using two kinds of negatively electrifiable silica fine particles each having a different particle size in an appropriate mass ratio.

[0129]

[Effect of the Invention]

A toner obtained by the external addition of, to toner mother particles, negatively electrifiable silica fine particles, titanium oxide fine particles, and

positively electrifiable silica fine particles in this order; negatively electrifiable silica fine particles, titanium oxide fine particles, positively electrifiable silica fine particles, and particles comprising a long chain fatty acid or a salt thereof in this order; or negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof in this order, is uniform in the electrification property, is restrained in the liberation of silica fine particles or titanium oxide fine particles, can maintain a stable electrification property for a long period of time, and is excellent in flowability.

[Designation of Document] ABSTRACT

[Abstract]

[Problem] To provide a toner which is low in desorption of silica fine particles or titanium oxide fine particles, which can maintain the electrification property for a long period of time, shows high flowability.

[Means for Solving the Problem] A toner obtained by the external addition of, to toner mother particles, negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles in this order; negatively electrifiable silica fine particles, titanium oxide fine particles, positively electrifiable silica fine particles, and particles comprising a long chain fatty acid or a salt thereof in this order; or negatively electrifiable silica fine particles, titanium oxide fine particles, and positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof in this order.

[Representative Drawing] none